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Description

Side-chain-modified copolymer waxes

- 5 The invention relates to side-chain-modified copolymer waxes composed of long-chain olefins, of acrylic esters, acrylic acid, and/or of acrylamides, to a process for their preparation, and also to their use.

10 Copolymers with varying proportion of ethylene and acrylic acid are widely used. They are characterized by a high proportion of linear hydrocarbon and by the acid function derived from the acrylic acid. Alongside ethylene, use is also made of other short-chain olefins and acrylic esters. Since these reaction products are preferably plastics-like polymers which have only limited accessibility to subsequent chemical reaction, the corresponding
 15 acrylic acid derivatives (such as esters or amides) have hitherto been used directly for the modification of the side chains.

For example, US-A-4,413,096 describes copolymers composed of ethylene and of acrylic esters derived from 2,2,6,6-tetramethylpiperidinol, their
 20 functionality enabling them to be used as light stabilizers.

DE 41 39 601 A1 describes copolymers composed of long-chain olefins with acrylic acid and methyl acrylate. As a result of the choice of the olefins, these products exhibit markedly waxy character. The side-chain
 25 functionality is limited to methyl or ethyl esters of acrylic acid.

It is desirable to find products which have waxy character but have an additional functionality in their side chains. It is known that products of this type can be prepared by copolymerizing long-chain olefins with the
 30 correspondingly modified acrylic acid derivatives. However, a number of disadvantages are attached to these processes. For example, acrylic acid derivatives of long-chain alcohols, of fluorinated alcohols, or of amines, are very expensive and complicated to prepare and purify. Furthermore, amine-containing derivatives undergo alteration in the presence of peroxides or of
 35 other free-radical initiators for the polymerization reaction, preventing preparation of the desired products. Other modified acrylic acid derivatives are very reluctant to form adducts with the respective olefin, or fail entirely to do so without undergoing alteration.

It is therefore an object of the present invention to provide copolymer waxes which can be modified in a particularly simple manner and which eliminate the disadvantages of the prior art. A further intention was to
5 provide access or, respectively, easy access to products which hitherto have been impossible or very difficult to prepare.

This object is achieved via side-chain-modified copolymer waxes of the type mentioned at the outset, which are prepared from waxy copolymers of
10 long-chain α -olefins having from 18 to 60 carbon atoms, methyl acrylate, acrylic acid, and/or from acrylamides whose carboxy functionality has been modified via chemical reaction with nucleophilic components.

The nucleophilic components are preferably long-chain alcohols, perfluoroalkyl alcohols, short-chain amines, long-chain amines, and/or
15 amino alcohols.

The long-chain alcohols are preferably tallow fatty alcohol, coconut fatty alcohol, oxo alcohols, and/or Guerbet alcohol.
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The perfluoro alcohols are preferably C₈-C₁₈-perfluoroalkylpropanol and distillate cuts of these alcohols.

Distillate cut: distillation is a physical separation method in which the different boiling points of the constituents (components) of a mixture are
25 utilized for separation. In its simplest variant, the liquid dripping down from the condenser is collected successively and separately in small fractions. This procedure is continued until most of the original volume has been distilled. A suitable method is then used to study the composition of the individual fractions. These fractions are also termed distillation cut (distillate
30 cut). The composition of these fractions depends on the boiling point differences of the individual components and on the distillation conditions.

The short-chain amines are preferably butylamine, dimethylaminopropylamine, diethylaminoethanol, tetramethylpiperidinol and/or triacetone-
35 diamine.

The long-chain amines are preferably octylamine, decylamine, dodecylamine, tallow fatty amine, coconut fatty amine, didecylamine, and/or cyclohexylamine. In industry, long-chain compounds are usually

those having alkyl chain lengths > C8, for example those found in wetting agents, surfactants, and waxes. This term may include not only linear aliphatic substances but also branched aliphatic and cycloaliphatic substances.

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The alkanolamines are preferably diethylaminoethanol, 2,2,6,6-tetramethylpiperidinol, N-methyl-2,2,6,6-tetramethylpiperidinol, N-acetyl-2,2,6,6-tetramethylpiperidinol and/or 2,2,6,6-tetramethylpiperidinol N-oxide.

- 10 The present object is also achieved via a process for the production of side-chain-modified copolymer waxes which comprises first reacting long-chain alpha-olefins having from 18 to 60 carbon atoms with acrylic esters, acrylic acid, and/or with acrylamides, to give long-chain copolymer waxes, and then reacting these with nucleophilic components to give the side-
- 15 chain-modified copolymer waxes.

The nucleophilic components which can be used for the abovementioned process are preferably long-chain alcohols, such as tallow fatty alcohol, coconut fatty alcohol, oxo alcohols, and/or Guerbet alcohol; perfluoroalkyl

20 alcohol, such as C₈-C₁₈-perfluoroalkylpropanol, and distillate cuts of these alcohols; short-chain amines, such as butylamine, dimethylamino-propylamine, diethylaminoethanol, tetramethylpiperidinol, and/or triacetonediamine; long-chain amines, such as octylamine, decylamine, dodecylamine, tallow fatty amine, coconut fatty amine, didecylamine,

25 and/or cyclohexylamine, and/or alkanolamines, such as diethylaminoethanol, 2,2,6,6-tetramethylpiperidinol, N-methyl-2,2,6,6-tetramethylpiperidinol, N-acetyl-2,2,6,6-tetramethylpiperidinol and/or 2,2,6,6-tetramethylpiperidinol N-oxide.

- 30 The invention also provides the use of the inventive side-chain-modified copolymer waxes in emulsified form for coatings and water-repellency.

The side-chain-modified copolymer waxes are also used in micronized form as matting agents, slip agents, antiscratch agents, and for improving

35 chemicals resistance.

They are likewise used in the form of lubricants, dispersing agent, or light stabilizer, as processing aids for plastics.

The term carboxy functionality is explained as follows:

Copolymerization of olefins with acrylic acid and with acrylic esters gives polymers which contain carboxylic acid functions and contain ester functions.

- 5 These functions are usually termed carboxy functions. In the raw materials, it is the functionality of the acid COOH and of the methyl ester COOCH_3 that are altered in the inventive reaction products to give COOR and CONR^1R^2 . R here are alkyl groups other than CH_3 .
- 10 The invention is explained via the following examples. The determination methods used were as follows:

- Drop point	DIN 51801/2, ASTM D 127
- Softening point	DIN EN 1427, ASTM E 28, ASTM D 36
- Acid number	DIN 53402, ASTM 1386
- Saponification number	DIN 53401 ASTM 1387
- Density	DIN 53479 ASTM D 1298, D 1505
- Viscosity	DIN 51562 DIN 53018
- Hydroxy number	OHZ DGF M IV 6 (57)

Preparation examples

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Comparative example 1:

Copolymer composed of C_{30} - α -olefins with acrylic acid/methyl acrylate

Mixture:

C_{30} - α -olefin	1 mol
Acrylic acid	0.3 mol
Methyl acrylate	2.5 mol
Di-tert-butyl peroxide	5% by weight, based on methyl acrylate

20 Process:

The olefin is melted at 100°C , and the mixture is heated to 150°C , and then di-tert-butyl peroxide, methyl acrylate, and acrylic acid are metered in, and stirring is continued for 5 hours. The free monomers are removed by distillation.

Acid number:	5
Viscosity number (cm ³ /g):	149
Drop point (°C):	76.5
Molecular weight:	about 3000

Comparative example 2:

- 5 Copolymer composed of C₂₀/C₂₂- α -olefin with methyl acrylate

Mixture:

C ₂₀ /C ₂₂ - α -olefin	1 mol
Acrylic acid	0.1 mol
Methyl acrylate	1.5 mol
Di-tert-butyl peroxide	5% by weight, based on methyl acrylate

Process:

- 10 The olefin is melted at 100°C, and the mixture is heated to 150°C, and then di-tert-butyl peroxide, methyl acrylate, and acrylic acid are metered in, and stirring is continued for 5 hours. The free monomers are removed by distillation.

Acid number:	15
Viscosity number (cm ³ /g):	180
Drop point (°C):	56.5
Molecular weight:	about 5000

- 15 Comparative example 3:
Copolymer composed of C₃₀- α -olefin with methyl acrylate

Mixture:

C ₃₀ - α -olefin	1 mol
Methyl acrylate	1.5 mol
Di-tert-butyl peroxide	5% by weight, based on methyl acrylate

Process:

- 20 The olefin is melted at 100°C, and the mixture is heated to 150°C, and then di-tert-butyl peroxide and methyl acrylate are metered in, and stirring is continued for 3 hours. The free monomers are removed by distillation.

Acid number:	1
Viscosity number (cm ³ /g):	101
Drop point (°C):	71.3
Molecular weight:	about 3500

Comparative example 4:

Copolymer composed of C₁₈- α -olefin with methyl acrylate

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Mixture:

C ₁₈ - α -olefin	1 mol
Methyl acrylate	2.5 mol
Di-tert-butyl peroxide	5% by weight, based on methyl acrylate

Process:

The olefin is melted at 100°C, and the mixture is heated to 150°C, and then di-tert-butyl peroxide and methyl acrylate are metered in, and stirring is continued for 5 hours. The free monomers are removed by distillation.

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Acid number:	1
Viscosity number (cm ³ /g):	385
Drop point (°C):	46.5
Molecular weight:	about 5000
Melt viscosity (160°C):	2060 mPas

15 Inventive examples:

Inventive example 1: Copolymer wax modified with tallow fatty alcohol side chains

Copolymer of comparative example 3	1 mol,
Tallow fatty alcohol	0.5 mol,
Na methoxide	0.3% by weight, based on mixture

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Process:

The copolymer is melted at 100°C, treated with the catalyst (Na methoxide) and with the alcohol component (tallow fatty alcohol), and heated to 180°C.

The mixture is stirred at this temperature for 7 hours, and methanol liberated is removed by distillation. Vacuum is then applied in order to remove residues of methanol and other alcohols by distillation, phosphoric acid is used for neutralization, and the mixture is cooled to 120°C and filtered.

Acid number:	10
Viscosity number (cm ³ /g):	80
Drop point (°C):	74.3

The product is a suitable lubricant for PVC with pale color and polarity adjustable by way of the degree of exchange, and is also a suitable dispersion aid for pigments.

Inventive example 2:

Copolymer wax modified with perfluoroalkylpropanol (C₁₂-C₁₄) side chains

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Copolymer of comparative example 1	1 mol,
C ₁₂ -C ₁₄ -perfluoroalkylpropanol	0.12 mol,
Na methoxide	0.3% by weight, based on mixture

Process:

The copolymer is melted at 100°C, treated with the catalyst (Na methoxide) and with the alcohol component (C₁₂-C₁₄-perfluoroalkylpropanol), and heated to 180°C. The mixture is stirred at this temperature for 7 hours, and methanol liberated is removed by distillation. Vacuum is then applied in order to remove residues of methanol and other alcohols by distillation, phosphoric acid is used for neutralization, and the mixture is cooled to 120°C and filtered.

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Acid number:	10
Viscosity number (cm ³ /g):	145
Drop point (°C):	70.3
Melt viscosity (160 l):	572 mPas

The product is suitable for the preparation of emulsions with water repellency, car polishes, textile emulsions, and also for the preparation of

micronizates with about 10 micron particle size, and for providing gloss and slip in aqueous and solvent-based coatings.

Emulsion formulation:

Experimental wax of inventive example 3	5.0 g
®Licowax KSL	15.0 g
Wax emulsifier 4106	3.0 g
Olein	1.0 g
KOH	0.4 g
Water	75.6 g

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Coating formulation:

KPU coating	98.0 g
Wax of example 2, micronized	2.0 g

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Gloss at 60°C

55 units, compared with 140 without addition = good matting

Sliding friction with 0.914 kg load

15 0.16 g, compared with 0.35 g without addition = good scuff protection

Water and alcohol resistance

No solvation, compared with discernible solvation without addition

= good water and alcohol
resistance

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Inventive example 3:

Copolymer wax modified with triacetonediamine side chains

Copolymer of comparative example 1	1 mol
Triacetonediamine	0.25 mol
®Fascacat 4102	0.2% by weight based on mixture

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Process:

The copolymer is melted at 100°C, treated with the catalyst (®Fascacat 4102) and with the amine component, and heated to 190°C. The mixture is stirred at this temperature for 7 hours, and methanol liberated is removed by distillation. Vacuum is then applied in order to remove residues of methanol

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and amine by distillation, and the mixture is cooled to 120°C and filtered.

Acid number:	10
Viscosity number (cm ³ /g):	145
Drop point (°C):	70.3
Melt viscosity (100°C):	572 mPas

5 Recommended application:

Light stabilizer for very thin polypropylene applications, tape products with reduced water adhesion.

Performance test

- 10 water carry-over effect = wco (quantitative evaluation of water absorption during the production process, the method of evaluation using a scale from 1 to 5)

*Mosten 58.412 polypropylene + 0.15 parts of auxiliary

- 15 *(Czech polypropylene)
extruded to give tapes with film thickness 100 microns
Extruder: 270°C, 92 rpm, 4 m/min

	®Chimasorb 944	wco value 5
20	®Hostavin N 24	wco value 4
	®Tunuvin 622	wco value 2
	Experimental product according to example 3	wco value 0

- 25 A scale from 0 to 5 was used for evaluation, where 0 = no water absorption and 1-5 is rising water absorption, industrial use being assessed as impossible from 3 upward.

Inventive example 4:

- 30 Copolymer wax side-chain-modified with triacetonediamine

Copolymer of comparative example 4	1 mol
Triacetonediamine	0.5 mol
®Fascat 4102	0.2% by weight based on mixture

Process:

- The copolymer is melted at 100°C, treated with the catalyst (®Fascat 4102) and with the amine component, and heated to 190°C. The mixture is stirred at this temperature for 7 hours, and methanol liberated is removed by distillation. Vacuum is then applied in order to remove residues of methanol and amine by distillation, and the mixture is cooled to 150°C and filtered.

Acid number: 18
 Viscosity number (cm³/g): 136
 Drop point (°C): 120°C
 Alkali number: 67.8
 Melt viscosity (170°C): 572 mPas

Recommended application:

- Processing aid for polyolefins and pigment dispersion with light-stabilizer action.

Performance test

- 0.1 mm films pressed from PP with 0.15% of a active substance or a active substance equivalent

Active substance	Time to decomposition in hours
®Hostavin N20	2100
®Hostavin N30	2000
®Cimasorb 944	2000
®Tinuvin 770	1400
Experimental product of inventive example 4	2100

Inventive example 5:

Copolymer wax side-chain-modified with 2,2,6,6-tetramethylpiperidinol

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Copolymer of comparative example 1 1 mol
 2,2,6,6-tetramethylpiperidinol 0.6 mol
 ®Fascat 4102 0.2% by weight based on mixture

Process:

The copolymer is melted at 100°C, treated with the catalyst and with the amine component, and heated to 190°C. The mixture is stirred at this

temperature for 7 hours, and methanol liberated is removed by distillation. Vacuum is then applied in order to remove residues of methanol and amine by distillation, and the mixture is cooled to 150°C and filtered.

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Acid number:	8
Viscosity number (cm ³ /g):	136
Drop point (°C):	68
Alkali number:	21
Melt viscosity (170°C):	76 mPas

The product is used as processing aid in polypropylene with light-stabilizer action.

- 10 Inventive example 6:
Copolymer wax side-chain-modified with triacetonediamine

Copolymer of comparative example 1	1 mol
Triacetonediamine	0.6 mol
®Fascat 4102	0.2% by weight based on mixture

- 15 The copolymer is melted at 100°C, treated with the catalyst and with the amine component, and heated to 190°C. The mixture is stirred at this temperature for 7 hours, and methanol liberated is removed by distillation. Vacuum is then applied in order to remove residues of methanol and amine by distillation, and the mixture is cooled to 150°C and filtered.

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Acid number:	16
Viscosity number (cm ³ /g):	82
Drop point (°C):	113
Alkali number:	67.8
Melt viscosity (170°C):	572 mPas

Inventive example 7:
Copolymer wax side-chain-modified with diethylaminopropylamine

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Copolymer of comparative example 4	1 mol
Diethylaminopropylamine	0.6 mol
®Fascat 4102	0.2% by weight based on mixture

- 5 The copolymer is melted at 100°C, treated with the catalyst and with the amine component, and heated to 190°C. The mixture is stirred at this temperature for 7 hours, and methanol liberated is removed by distillation. Vacuum is then applied in order to remove residues of methanol and amine by distillation, and the mixture is cooled to 150°C and filtered.

Acid number:	5
Viscosity number (cm ³ /g):	82
Drop point (°C):	118
Alkali number:	74
Melt viscosity (170°C):	572 mPas

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Recommended application:

Cationically emulsifiable wax for water-resistant coatings, car polishes, floorcoverings, crop protection

- 15 Formulation:

Experimental wax of inventive example 7	22.5 g
Wax emulsifier	2.25 g
Acetic acid	1.5 g
Water	73.75 g

Inventive example 8:

Copolymer wax side-chain-modified with octylamine

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Copolymer of comparative example 1	1 mol
Octylamine	0.6 mol
®Fascat 4102	0.2% by weight based on mixture

The copolymer is melted at 100°C, treated with the catalyst and with the amine component, and heated to 190°C. The mixture is stirred at this temperature for 7 hours, and methanol liberated is removed by distillation.

Vacuum is then applied in order to remove residues of methanol and amine by distillation, and the mixture is cooled to 150°C and filtered.

Acid number:	16
Viscosity number (cm ³ /g):	45
Drop point (°C):	95
Alkali number:	3
Melt viscosity (170°C):	360 mPas

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Dispersing agent in engineering thermoplastics

Summary of inventive examples:

- 10 Copolymers available in the prior art are in essence based on reactions of ethylene or of long-chain olefins with acrylic acid or with acrylic esters. In the case of ethylene, these are plastics which cannot be further modified, and in the case of the long-chain olefins they are waxy compounds. The prior art achieves functionality via incorporation of appropriate acrylic acid
- 15 derivatives, e.g. stearyl acrylate, 2,2,6,6-tetramethylpiperidiny acrylate, perfluoroalkyl acrylate, N-octylacrylamide, etc.

- 20 A more cost-effective method giving easier control of functionality is the chemical modification of waxy copolymers composed of long-chain olefins and acrylic acid compounds as claimed in the present invention. Suitable conduct of the reaction here can react to the acrylic acid compound with the desired functional components. This permits preparation of waxy polymers (copolymer waxes) for a wide variety of applications.